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G2C C9H2 C9H3A1C C9H3B1 C9H3B2A C9H3B2C C9H3B3A C9H3B3B C9H3B3F C9H3C1 C9P1F C9P3

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(54) PHOTOGRAPHIC SILVER HALIDE ELEMENT

(71) We, AGFA-GEVAERT, a Naamloze Vennootschap organised under the laws of Belgium, of 27 Septestraat, 2510 Mortsel, Belgium, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: —

The present invention relates to photographic silver halide elements having outer coatings with improved surface and antistatic properties.

It is known that discrete solid particles of water-insoluble inorganic or organic materials, called matting agents, can be used in a protective layer over the silver halide emulsion layer of a photographic element and/or in a backing layer at the rear of the support of said element to provide rough surfaces which are often desirable in the photographic art. Examples of inorganic matting agents are silicon dioxide, titanium dioxide, magnesium oxide, aluminium oxide, barium sulphate, calcium carbonate, glass, etc. Examples of organic matting agents are starch, cellulose esters such as cellulose acetate propionate, cellulose ethers such as ethyl cellulose, synthetic resins such as polymeric esters of acrylic and methacrylic acid for example polymethyl methacrylate, polyvinyl resins such as polyvinyl acetate, polycarbonates, homo- and copolymers of styrene, etc. These matting agents may be used in order to reduce the sticking tendency of the photographic material for example when the material is stored or packed in the form of a roll or stack. They may be used to provide sufficient surface roughness to prevent the formation of Newton's rings when printing and enlarging in that the contact surface of the photographic material with another material is relatively small. Further, they may be used to decrease abrasion by dry-friction and to reduce the tendency of scratching when materials are stored or packed in contact with other material as is the case e.g. with X-ray material packed without interleaves. It is also possible to use matting agents in order to obtain the desired coefficient of friction for film materials intended for use in apparatus for rapid handling and transport. Moreover, matting agents may have in some cases a slight effect in reducing the generation of static electricity in photographic elements, since a rough surface is obtained and therefore the contacting surface of the photographic element with other materials, which might cause static discharges, is reduced.

Owing to the generation of static electricity a large number of difficulties are encountered during the preparation and use of photographic elements, especially film elements. The generation of static electricity may be caused by rubbing of the film element against rollers and other elements through or on which the film materials are guided, by contact of the film element with rough surfaces or by many other known reasons. Discharges of static electricity in an unprocessed photographic element cause local film exposure and on processing said element the discharge images becomes visible in the form of irregular streaks or lines and black spots. Discharges in a processed film element, especially in film material for cinematographic purposes, are also undesirable since friction of the film material against elements of the projection apparatus is thereby enhanced.

Matting agents have a poor antistatic effect and therefore if it is the intention to effectively reduce the generation of static electricity, the outer coatings provided as protective coating over a radiation-sensitive silver halide emulsion layer or as backing

layer at the rear of the support generally comprise compounds known as antistatic agents.

Antistatic agents, however, have an influence on the coating characteristics of the hydrophilic colloid composition when used therein; for instance they may reduce the coating quality such as the uniformity of coating and may give rise to the formation of streaks and repellency spots or comets. The coating quality can, of course, be improved by appropriate choice of surface active compounds as the coating acid such as saponine, aliphatic sulphate, sulphonates and carboxylates, which may comprise alkylene oxide units, etc. but these coating aids in their turn often reduce the antistatic properties of the hydrophilic colloid coating in which they are incorporated.

In Belgian Patent Specification No. 742,680 fluorinated surfactants have been described for use as coating aids in hydrophilic colloid coating compositions. By the use of these fluorinated surfactants instead of known coating aids or in addition thereto it was found possible to reduce or eliminate the disadvantageous effect of known coating aids on the antistatic properties while retaining favourable coating qualities.

It has now been found that the favourable effect of these fluorinated surfactants in reducing the generation of static electricity in a hydrophilic colloid outer coating of a photographic silver halide element, can still be improved by addition of solid water-insoluble particles of matting agents to the coating composition of the said outer coating.

We found that the simultaneous use in photographic silver halide elements of matting agents, which themselves have only a poor antistatic effect, and fluorinated surfactants, which have better antistatic properties than matting agents, could provide substantially superior antistatic properties than was to be expected knowing the effects of both agents alone. This is illustrated in the Examples hereinafter.

By the combined use of a matting agent and a fluorinated surfactant optimum triboelectric properties are obtained for the photographic element with regard to conventional materials such as paper, stainless steel, rubber, synthetic resins, etc. that come into contact with the said element.

In accordance with the present invention there is provided a photographic radiation-sensitive silver halide element, which comprises a radiation-sensitive silver halide emulsion layer an an outer coating of a hydrophilic colloid, wherien the said outer coating comprises a fluorinated surfactant as well as a matting agent.

The invention is especially concerned with the improvement of the antistatic properties of hydrophilic colloid protective coatings coated over a radiation-sensitive silver halide emulsion layer and is of particular value in the manufacture of X-ray material, more especially double coated X-ray material and other double coated films where both sides of the film support e.g. a cellulose triacetate or polyethylene terephthalate support are provided with radiation-sensitive silver halide emulsion layers and hydrophilic colloid protective coatings as outer layers.

The matting agents of use according to the present invention may be of inorganic as well as organic nature, examples of which have been given before. It is also possible to use a combination of at least two different matting agents for instance matting agents differing from one another in hardness, one being relatively soft such as polymethylmethacrylate and another being relatively hard such as silicon dioxide.

The matting agents of use according to the present invention are incorporated into the hydrophilic colloid coating composition of the outer coating, more especially a protective coating to be applied over the photographic silver halide emulsion layer, using any method which will achieve uniform dispersion of the particles in the layer. The matting agents may be used in amounts varying between very wide limits. In general, the matting agents can be used, per side of support, at a total coverage in the range of about 10 mg to about 100 mg per sq.m, although larger amounts may also be used. The matting agent particles generally have a particle diameter comprised between 1 and 10 microns, preferably at least 50 % of the matting agent particles have a diameter in the range of 4 to 7 microns.

Photographic elements containing matting agents in an outer layer generally exhibit especially good resistance to abrasion, a reduced sticking tendency of the element when it is stored or packed in the form of a roll or stack and a favourable coefficient of friction for use in apparatus for rapid handling and transport. However, the presence of matting agent particles in such an outer layer sometimes causes turbidity so that a processed silver image has a milky appearance. This situation can be corrected by incorporating into the outer layer polycarbocyclic aromatic sulphonic acids or water-soluble salts thereof as described in Belgian Patent Specification 738,856.

The hydrophilic colloid of the outer coating preferably comprises gelatin as hydrophilic colloid though other hydrophilic colloidal materials or mixtures of them, e.g.

hydrophilic natural colloids, modified hydrophilic natural colloids or synthetic hydrophilic polymers may also be used. More particularly these colloids may be selected of such film-forming natural or modified natural hydrophilic colloids as e.g. glue, casein, zein, hydroxyethyl cellulose, carboxymethyl cellulose, methyl cellulose, carboxymethyl hydroxyethyl cellulose, gum arabic, sodium alginate and hydrophilic derivatives of such colloids. They may also be selected of such synthetic hydrophilic polymers as e.g. polyvinyl alcohol, poly-N-vinyl pyrrolidone, polyvinyl amine, polyethylene oxide, polystyrene sulphonic acid, polyacrylic acid, and hydrophilic copolymers and derivatives of such polymers.

The fluorinated surfactants for use in accordance with the present invention comprise, as described in Belgian Patent Specification 742,680, one or more hydrocarbon chain(s), at least one of which is a C_3—C_{20} hydrophobic hydrocarbon chain, and at least one hydrophilic anionic group, hydrophilic non-ionic group or hydrophilic betaine group, and are characterized by the fact that the hydrogen atoms of one or more of the said hydrocarbon chain(s) are wholly or partly replaced by fluorine. They can be represented by the formula:

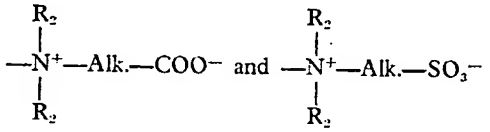
$$R_F—A—X$$

wherein:

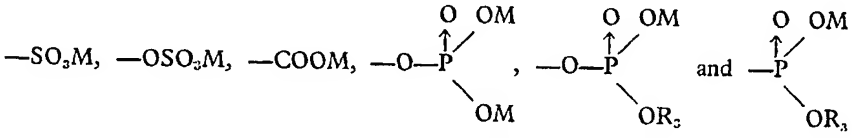
R_F stands for a partly or wholly fluorinated hydrocarbon chain comprising at least 3 fluorine atoms.

A stands for a chemical bond or a bivalent hydrocarbon group, preferably an aliphatic, aromatic or mixed aliphatic-aromatic group including such bivalent hydrocarbon group interrupted by heteroatoms, such as oxygen, ester groups (—COO—) and amide groups (—CONR— and —SO_2NR— wherein R is H or C_1—C_5 alkyl), and

X stands for a hydrophilic group for example a hydrophilic non-ionic polyoxyalkylene group such as a polyoxyethylene group of the formula $(—CH_2CH_2O)_nR_1$ wherein R_1 stands for hydrogen or alkyl comprising from 1 to 5 carbon atoms such as methyl and n stands for an integer from 5 to 20 which polyoxyethylene group may be interrupted by one or more isopropyleneoxy groups, a hydrophilic betaine group such as the groups



wherein Alk. stands for C_1—C_5 alkylene group such as methylene, ethylene, propylene and butylene and R_2 stands for C_1—C_5 alkyl group such as methyl and ethyl, and preferably a hydrophilic anionic group such as the groups



wherein M stands for hydrogen, an alkali metal atom such as sodium and potassium, an ammonium group or an organic ammonium group such as diethanolammonium, morpholinium, pyridinium etc. and R_3 stands for an alkyl group or the group R_F.

The sum of the number of F-atoms, in the group R_F plus the number of C-atoms in the fluorinated hydrocarbon chain of R_F and the number of C-atoms in the hydrocarbon group of A (if any) is preferably at least equal to 10. In accordance with the present invention best results are obtained with fluorinated surfactants having a terminal trifluoromethyl group.

Representative examples of fluorinated surfactants suitable for use according to the present invention and corresponding to the above general formula are:

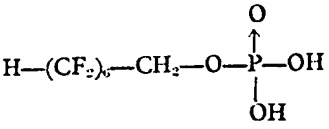
1. $F_3C—(CF_2)_2—COOH$
2. $H—(CF_2)_6—COOH$
3. $CF_3—(CF_2)_6—COONH_4$

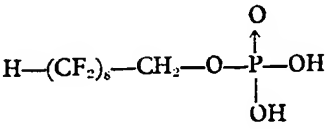
4. $H-(CF_2)_{10}-COOH$

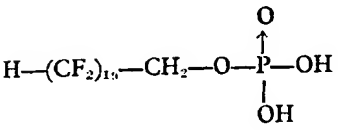
5. $F_3C-(CF_2)_7-SO_3K$

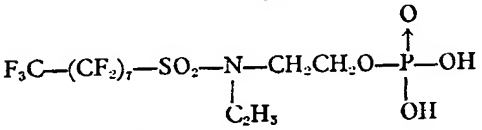
6. $H-(CF_2)_6-CH_2-OSO_3Na$

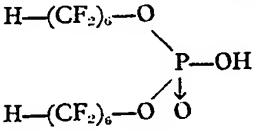
7. $H-(CF_2)_8-CH_2-OSO_3Na$

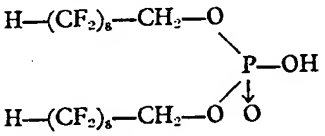
8. 

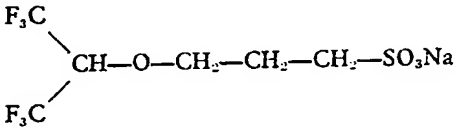
9. 

10. 

11. 

12. 

13. 

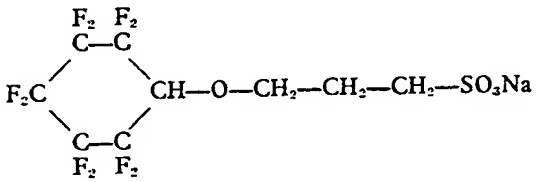
14. 

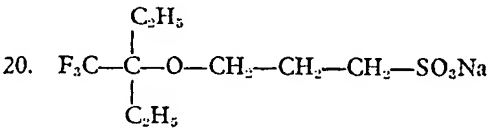
15. $H-(CF_2)_6-CH_2-O-CH_2-CH_2-CH_2-SO_3Na$

16. $H-(CF_2)_8-CH_2-O-CH_2-CH_2-CH_2-SO_3Na$

17. $H-(CF_2)_{10}-CH_2-O-CH_2-CH_2-CH_2-SO_3Na$

18. $F_3C-(CF_2)_6-CH_2-O-CH_2-CH_2-CH_2-SO_3Na$

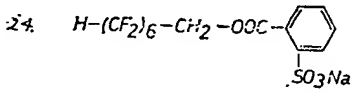
19. 

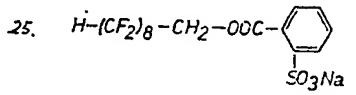
20. 

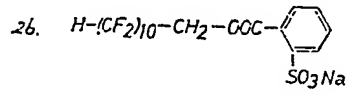
21. $F_3C—(CF_2)_2—COO—CH_2—CH_2—CH_2—SO_3Na$

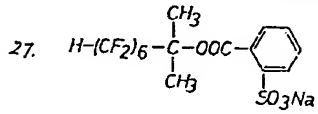
22. $H—(CF_2)_{10}—COO—CH_2—CH_2—CH_2—SO_3Na$

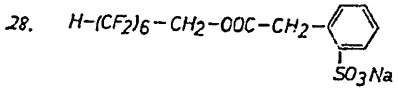
23. $H—(CF_2)_6—CH_2—OOC—CH_2—CH_2—SO_3Na$

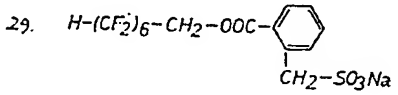
24. 

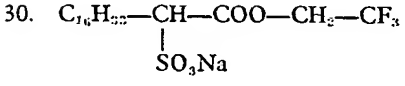
25. 

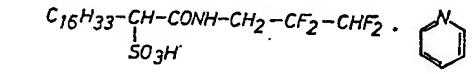
26. 

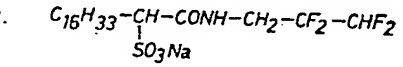
27. 

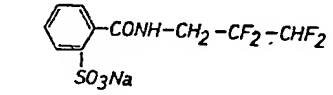
28. 

29. 

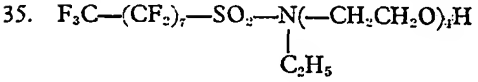
30. 

31. 

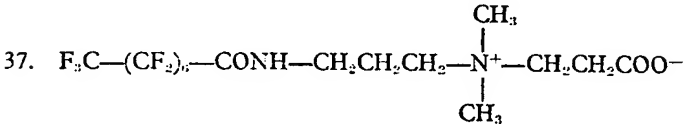
32. 

33. 

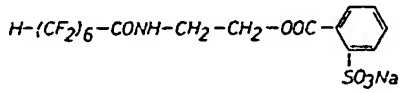
34. $F_3C—(CF_2)_2—COO(—CH_2CH_2O)_7—CH_3$

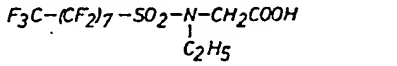
35. 

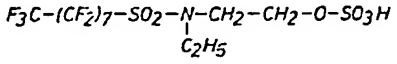
36. $F_3C—(CF_2)_2—CH_2O(—CH_2CH_2O)_5H$

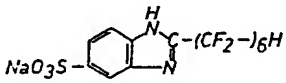
37. 

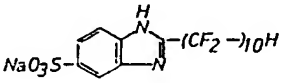
38. $H-(CF_2)_6-CONH-CH_2-CH_2-O-SO_3Na$

39. 

40. 

41. 

42. 

43. 

The fluorinated surfactants for use in combination with matting agents in order to improve the antistatic properties of hydrophilic colloid outer coatings need not necessarily be provided in the coating composition for forming said outer coating comprising the matting agent. As a matter of fact, it is also possible to incorporated the fluorinated surfactants in the coating composition of an underlying water-permeable colloid layer such as a silver halide emulsion from which they can diffuse to the surface of the outer coating when the composition for forming the latter is applied on the wet or gellified but not yet dried underlying layer. Alternatively, the fluorinated surfactant may be incorporated into both the coating composition for forming the outer coating and the coating composition for forming an underlying water-permeable colloid layer for instance both in the radiation-sensitive silver halide emulsion and the hydrophilic colloid coating compositions for being coated thereover.

The fluorinated surfactants are generally used in amounts comprised between 0.1 and 2 % by weight relative to the amount of dry colloid of the layer into which the said fluorinated surfactants are incorporated.

Protective colloid compositions for being coated over radiation-sensitive silver halide emulsion layers comprising matting agents and fluorinated surfactants, of which the latter can be present therein by direct incorporation or by diffusion from underlying silver halide emulsion layers may comprise all sorts of other materials conventionally used in said protective layers. For instance, they may comprise plasticizers, filling agents, hardening agents such as formaldehyde and mucochloric acid, hardening accelerators such as resorcin, polyvinyl lactams and polyvinyl lactones such as poly-N-vinyl pyrrolidone and polyvinyl-2-oxazolidone as antifoggants, antistatic agents e.g. polyoxyalkylene compounds for example alkoxylated alcohols and phenols such as ethoxylated alkyl phenols, ethoxylated castor oil, polyoxyalkylene esters of fatty acids such as the polyoxyethylene glycol (molecular weight about 300) ester of oleic acid, urethans or esters of the above alkoxylated hydroxy compounds e.g. those of the kind described in Belgian Patent Specification 706,563 such as the nonylphenoxy triethyleneoxyethyl ester of carbanilic acid. They may further comprise conventional coating aids such as saponine, dialkyl sulphosuccinic acid salts such as sodium diisooctylsulphosuccinate and salts of alkyl sulphuric acid, salts of alkyl sulphonic acids, salts of alkylaryl polyether sulphuric acids and salts of alkylaryl polyether sulphonic acids, carboxyalkylated polyethylene glycol ethers or esters, etc.

The silver halide employed in the preparation of the radiation-sensitive silver halide emulsion layer(s) of the photographic element according to the present invention includes any of the photographic silver halides as exemplified by silver bromide, silver iodide, silver chloride or mixed silver halides e.g. silver chlorobromide and silver bromoiodide.

The silver halides are dispersed in the common hydrophilic colloids or mixtures of colloids, examples of which are given above, gelatin being, however, favoured.

The support may be any conventional transparent or opaque support as normally used in the art such as paper, glass and film. The invention, however, is of particular advantage in those cases where transparent film supports are used such as films of

cellulose esters for instance cellulose triacetate, and films of polyester for instance polyethylene terephthalate.

The emulsion can contain the usual additives including for example, stabilizers or antifoggants such as inorganic acid salts of cadmium, cobalt and manganese and substituted triazoindolizines, speed increasing addenda such as alkylene oxide polymers and onium compounds for instance quaternary ammonium compounds, gelatin hardeners, plasticizers and the like. The emulsions may be spectrally sensitized emulsions as well as not spectrally sensitized emulsions.

The following examples illustrate the present invention.

Example 1

A gelatino silver bromoiodide (2 mole of iodide) X-ray emulsion comprising per kg 80 g of gelatin and an amount of silver halide corresponding to 190 g of silver nitrate was coated on both sides of a subbed cellulose triacetate support pro rata of about 27 sq.m (per side of support) per kg of emulsion.

At both sides of the support, the emulsion layers while still wet were overcoated with a gelatin antistress layer from an aqueous gelatin composition comprising per litre 30 g of gelatin, 28 ml of a 5 % aqueous solution of sodium diisooctyl sulphosuccinate as coating aid, an antistatic agent as well as the additives listed in the table below.

The gelatin antistress layers were coated pro rata of about 27 sq.m per litre of aqueous gelatin composition which means that per sq.m and per side of support about 1.1 g of gelatin was present.

The antistatic properties of the antistress layers were determined on the one hand by measuring the triboelectric charging of the photographic X-ray film material by rubbing against rubber, packaging or interleave paper and brass (the values listed in the table for this triboelectric charging are expressed in pico Coulomb) and on the other hand by estimating the discharge images produced in the emulsion layer by the sparks formed on rubbing the material against rubber, brass, polyvinyl chloride and intensifying lead screens. For the latter purpose, the light-sensitive material is rubbed against rubber, brass, polyvinyl chloride and intensifying lead screens in the dark whereupon the light-sensitive material is developed to make visible the discharge images produced. The values given for the sparks should be interpreted as follows: 0 stands for excellent, 1 stands for very good, 2 stands for good, 3 stands for unsatisfactory and 4 stands for poor behaviour against formation of sparks.

The results attained are listed in the Table I.

TABLE I

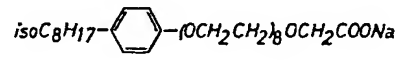
Additives to antistress layer per litre	Triboelectric charging (pico Coulomb) by rubbing against			Sparks
	brass	rubber	paper	
—	1100	700	−4500	4
1 g of polymethylmethacrylate particles 50% of which have a diameter of about 5 microns (A)	1000	1000	−3500	3
3 ml of a 5% aqueous solution of a mixture of perfluorocarboxylic acid ammonium salts substantially consisting of Compound 3 (B)	1000	600	−11000	3
(A) + (B)	300	500	−12000	1—2

The above results clearly show the unexpectable, favourable effect on the electrostatic properties of the combination of matting agents with fluorinated surfactants. For instance, while both the polymethylmethacrylate and the fluorinated surfactant have only a slight effect on the triboelectric charging by rubbing against brass, this charging is markedly reduced by using both agents together. Though, on rubbing against rubber, the matting agent increases the chargeability, the overall effect of the use of both agents together results in a reduction of the triboelectric charging which is higher than the reduction obtained with the fluorinated surfactant alone. The same favourable effect occurs when using as fluorinated surfactant compounds 4, 22, 24 and 25.

Example 2

This example shows that the same effects as described in Example 1 are obtained when the fluorinated surfactant is incorporated in the silver halide emulsion layer.

A silver bromoiodide X-ray emulsion comprising per kg 80 g of gelatin, an amount of silver halide corresponding to 190 g of silver nitrate and 6 ml of a 5 % aqueous solution of the coating aid with formula



was coated on both sides of a subbed cellulose triacetate support pro rata of about 27 sq.m (per side of support) per kg of emulsion.

At both sides of the support, the emulsion layers, while still wet, were overcoated with a gelatin antistress layer from an aqueous composition comprising per litre 30 g of gelatin, 28 ml of a 5 % aqueous solution of sodium diisooctylsulphosuccinate as coating aid, and an antistatic agent.

The gelatin antistress layers were coated pro rata of about 27 sq.m per litre of aqueous gelatin composition which means that per sq.m and per side of support about 1.1 g of gelatin was present.

The antistatic properties of the material A thus obtained were compared with the antistatic properties of a material B prepared in the same way with the only difference that the antistress coating composition also comprised per litre, 1 g of polymethylmethacrylate particles as described in example 1 and with the antistatic properties of a material C prepared in the same way as material B but with the further difference that the silver halide emulsion comprised per kg 2 ml of a 5% aqueous solution of the fluorinated surfactant referred to in the table of Example 1.

The results obtained are shown in Table II.

TABLE II

Material	Triboelectric charging (pico Coulomb) by rubbing against		
	brass	rubber	intensifying lead screens
A	8100	27000	1100
B	7900	28000	1200
C	4300	19000	−1500

WHAT WE CLAIM IS:—

1. A photographic element comprising a radiation-sensitive silver halide emulsion layer and a hydrophilic colloid outer layer wherein said outer layer comprises a fluorinated surfactant as well as solid, water-insoluble discrete particles of at least one matting agent.

2. A photographic element according to claim 1, wherein the particles of said matting agent(s) have a diameter comprised between 1 and 10 microns.

3. A photographic element according to claim 1 or 2, wherein at least 50 % of the said particles have a diameter in the range of 4 to 7 microns.

4. A photographic element according to claim 1 or 2, wherein polymethylmethacrylate is used as matting agent.

5. A photographic element according to any of claims 1 to 4, wherein said matting agent(s) is (are) used at a total coverage per side of the support, in the range of 10 mg to 100 mg per sq.m.

6. A photographic element according to any of claims 1 to 5, wherein said fluorinated surfactant comprises one or more hydrocarbon chain(s) at least one of which is a C_3 to C_{20} hydrophobic hydrocarbon chain, and at least one hydrophilic anionic group, hydrophilic non-ionic group or hydrophilic betaine group characterized in that the hydrogen atoms of one or more of the said hydrocarbon chain(s) are wholly or partly replaced by fluorine.

7. A photographic element according to claim 6, wherein said fluorinated surfactant corresponds to the formula:

$$R_F—A—X$$

wherein:

R_F stands for a partly or wholly fluorinated hydrocarbon chain comprising at least 3 fluorine atoms,

A stands for a chemical bond or a bivalent hydrocarbon group including a bivalent hydrocarbon group interrupted by one or more hetero atoms or by the group —COO—, —CON(R)— or —SO_2N(R)— wherein R is hydrogen or alkyl comprising from 1 to 5 C-atoms,

X stands for a hydrophilic non-ionic polyoxyalkylene group, a hydrophilic anionic group selected from

$$—SO_3M,\ —OSO_3M,\ —COOM,\ —O—\overset{\overset{O}{\uparrow}}{\underset{\underset{OM}{|}}{P}}—OM,\ —O—\overset{\overset{O}{\uparrow}}{\underset{\underset{OR_3}{|}}{P}}—OM \text{ and } —\overset{\overset{O}{\uparrow}}{\underset{\underset{OR_3}{|}}{P}}—OM$$

wherein M stands for hydrogen, an alkali metal atom, an ammonium group or an organic ammonium group and R_3 stands for an alkyl group or the group R_F, or a hydrophilic betaïne group selected from the group consisting of

$$—\overset{\overset{R_2}{|}}{\underset{\underset{R_2}{|}}{{}^{+}N}}—Alk.—COO^- \text{ and } —\overset{\overset{R_2}{|}}{\underset{\underset{R_2}{|}}{{}^{+}N}}—Alk.—SO_3^-$$

wherein R_2 stands for a C_1—C_3 alkyl group and Alk. stands for a C_1—C_3 alkylene group.

8. A photographic element according to claim 7, wherein the sum of the number of F-atoms in the group R_F plus the number of C-atoms in the fluorinated hydrocarbon group of R_F and the number of C-atoms in the hydrocarbon group of A (if any) is at least equal to 10.

9. A photographic element according to any of claims 6 to 8, wherein the fluorinated surfactant comprises a terminal trifluormethyl group.

10. A photographic element according to claim 6, wherein said fluorinated surfactant is a perfluorocarboxylic acid in acid or salt form.

11. A photographic element according to any of the preceding claims wherein the fluorinated surfactant is present in the said outer layer in an amount comprised between 0.1 and 2 % by weight relative to the amount of dry colloid.

12. A photographic element according to any of the preceding claims wherein the hydrophilic colloid of the said outer layer is gelatin.

13. A photographic element according to any of the preceding claims wherein the said radiation-sensitive silver halide emulsion layer is a gelatino silver halide X-ray emulsion layer.

14. A photographic element according to any of the preceding claims wherein the said element is a double-coated X-ray film element provided at both sides of the film support with a said radiation-sensitive silver halide emulsion layer and a said hydrophilic colloïd outer layer coated over each of the said emulsion layers.

15. A photographic element according to claim 1 and substantially as described herein.

16. A photographic element according to claim 1 and substantially as described in the Examples herein.

17. A method of preparing a photographic element having a radiation-sensitive silver halide emulsion layer and a hydrophilic colloid outer layer, which comprises incorporating a fluorinated surfactant into the said outer layer or into an underlying hydrophilic colloid layer from which the said fluorinated surfactant can diffuse towards the surface of said outer layer, and incorporating solid, water-insoluble discrete particles of at least one matting agent into the said outer layer.

18. A method according to claim 17, wherein polymethylmethacrylate is used as matting agent.

19. A method according to claim 17, wherein said particles have a diameter comprised between 1 and 10 microns.

20. A method according to any of claims 17 to 19, wherein at least 50 % of the said particles have a diameter in the range of 4 to 7 microns.

21. A method according to any of claims 17 to 20, wherein the said matting agent(s) is (are) incorporated in the said outer layer at a total coverage per side of support, in the range of 10 mg to 100 mg per sq.m.

22. A method according to any of claims 17 to 21, wherein the said fluorinated surfactant is a fluorinated surfactant as defined in any of claims 6 to 10.

23. A method according to any of claims 17 to 22 wherein the fluorinated surfactant is incorporated into the said outer layer or the said underlying hydrophilic colloid layer in an amount comprised between 0.1 and 2% by weight relative to the amount of dry colloid.

24. A method according to claim 17 and substantially as described herein.

25. A method according to claim 17 and substantially as described in the Examples herein.

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